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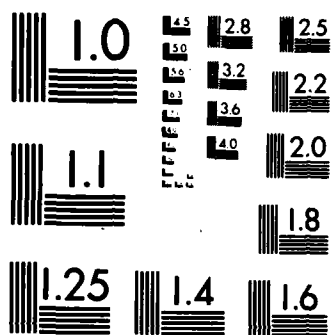
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Homogeneous Reaction Involving Components of
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By

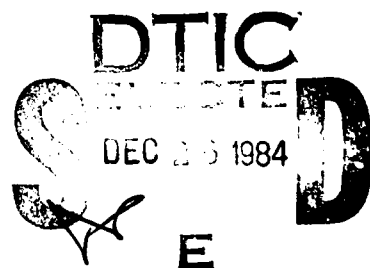
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HOMOGENEOUS REACTION INVOLVING COMPONENTS OF
DIFFERENT REDOX COUPLES. I. THEORETICAL
CONSIDERATIONS AND DIGITAL SIMULATION.

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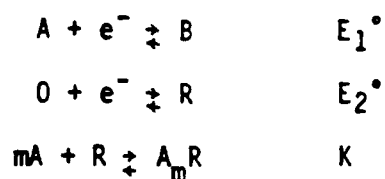


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ABSTRACT

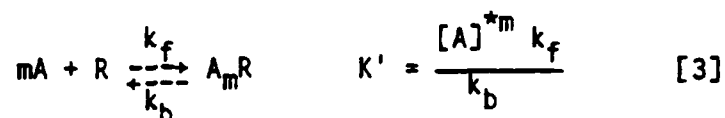
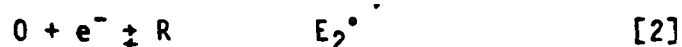
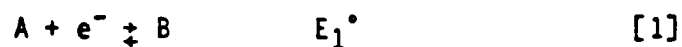
Coupled heterogeneous electron transfer/homogeneous reaction of the type



occur in the electrooxidation of certain anilines, and in association reactions of hydrocarbon anions with metal cations. If the adduct A_mR is electroinactive, the resulting voltammogram is distorted in a way which is characteristic of the value of m . The derivation of the theoretical fluxes for these reactions and calculated normal potential pulse voltammograms are presented. The results are derived from both limiting flux and digital simulation considerations.

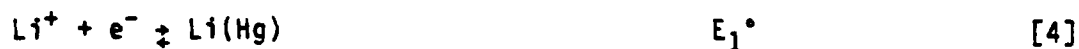
INTRODUCTION

We consider in this report a coupled sequence of heterogeneous electron transfer and homogeneous chemical reactions in which the chemical reactions involve the species of two different redox pairs.



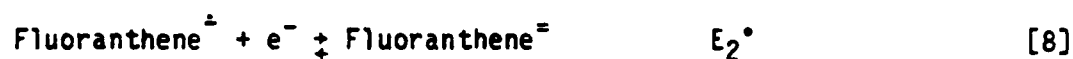
where $[A]^*$ is the bulk concentration of A.

Reactions second order and higher in A and/or R are also considered. Examples of these reactions include the reaction of hexaethylbenzene cation radical with hexamethylbenzene (1) and other hydrocarbons (2), and the compounds in part II (3) of this study, for example:



and





The voltammetry of these systems exhibits rather spectacular properties such as depression of faradaic currents to zero and in some circumstances formation of "pseudo" peaks and dips. These effects in the cyclic voltammetry of the hexaethylbenzene oxidations are explained by reaction with other electroactive hydrocarbons present wherein the second hydrocarbon concentration is therefore depleted. As a result, the flux of A to the electrode is reduced, resulting in current depression.

Unfortunately, analytical solutions for the current and concentration profiles are precluded by the non-linear form of the diffusion-kinetic equations which describe the reaction sequence [1]-[3]. Some predictions of the general behavior can be derived, however, and digital simulation of the system is quite straightforward, and provides details of the expected responses as a function of the usual parameters.

Theory

It is assumed that (a) B, R, and A_mR are electroinactive in the potential region considered and (b) A_mR is chemically stable. The experimental technique considered will be normal pulse voltammetry. This technique is useful in the study of systems where species A or O is an alkali metal ion (part II (3)). The alkali metal is then soluble in and deactivated chemically by the mercury drop, and is stable against interfering reaction with other system components. In the experiment, increasingly larger potential pulses are applied to new large mercury drop electrodes. The diffusion to such electrodes may be approximated as linear. The current transient is sampled at identical time intervals on each drop. The time interval is usually chosen so that charging current magnitudes have decayed to values well below the faradaic component so that their effect on the total current is minimized. The simulation of such an experiment is thus developed by considering a succession of chronoamperometric responses, each to slightly higher potential pulse values at a planar electrode. Corrections to the responses for sphericity effects for the cases considered herein proved to be less than 3% in the worst case, and will be neglected.

The partial differential equations describing the system [7]-[9] are

$$\frac{\partial[A]}{\partial t} = D_A \frac{\partial^2[A]}{\partial x^2} - mk_f[A]^m[R] + mk_b[A_mR] \quad [10]$$

$$\frac{\partial[O]}{\partial t} = D_O \frac{\partial^2[O]}{\partial x^2} \quad [11]$$

$$\frac{\partial[R]}{\partial t} = D_R \frac{\partial^2[R]}{\partial x^2} - m k_f[A]^m[R] + m k_b[A_mR] \quad [12]$$

$$\frac{\partial[A_mR]}{\partial t} = D_{A_mR} \frac{\partial^2[A_mR]}{\partial x^2} + mk_f[A]^m[R] - mk_b[A_mR] \quad [13]$$

where T , X , and D_i are time, distance from the electrode surface, and diffusion coefficients of the i th species, respectively.

The conditions for the experiment are summarized as:

Initial ($T = 0$):

$$\text{All } X: [A] = [A]^*, [O] = [O]^*, [R] = [A_m R] = 0 \quad [14]$$

Boundary:

$$T > 0, X = 0: [A]^\sigma = [B]^\sigma \exp [F(E - E_1^0)/RT] = \delta_1 \quad [15]$$

$$[O]^\sigma = [R]^\sigma \exp [F(E - E_2^0)/RT] = \delta_2 \quad [16]$$

(σ represents surface, $X = 0$)

$$D_A \left(\frac{\partial [A]}{\partial X} \right)_{X=0} = -D_B \left(\frac{\partial [B]}{\partial X} \right)_{X=0} \quad [17]$$

$$D_O \left(\frac{\partial [O]}{\partial X} \right)_{X=0} = -D_R \left(\frac{\partial [R]}{\partial X} \right)_{X=0} \quad [18]$$

$$i = FA [D_A \left(\frac{\partial [A]}{\partial X} \right)_{X=0} + D_O \left(\frac{\partial [O]}{\partial X} \right)_{X=0}] \quad [19]$$

$T > 0, X = \infty$:

$$\text{idem [14]} \quad [20]$$

The Cottrell currents at any potential for the processes [7] and [8] in the absence of any homogeneous reactions are given by

$$i_A = FAD_A^{1/2} [A]^b \left[\left(1 + \left(\frac{D_A}{D_B} \right)^{1/2} \delta_1 \right) \pi^{1/2} T^{1/2} \right]^{-1} \quad [21]$$

where A is the electrode area.

and

$$i_O = FAD_O^{1/2} [O]^* \left[\left(1 + \left(\frac{D_O}{D_R} \right)^{1/2} \delta_2 \right) \pi^{1/2} T^{1/2} \right]^{-1} \quad [22]$$

The sum of these two currents represents the total Cottrell current at any potential. The actual current for the kinetic system will, however, be affected by the decrease in [A] near the electrode due to the chemical reaction [9].

We define the following dimensionless parameters:

$$t = \frac{T}{\tau}, \quad \tau = \text{The chronoamperometric pulse width in seconds} \quad [23]$$

$$[A]^* = C_A^*, \quad \alpha = \frac{C_O^*}{C_A^*}, \quad C_O = \frac{[O]}{C_A^*}, \quad C_A = \frac{[A]}{C_A^*}$$

$$C_R = \frac{[R]}{C_A^*}, \quad C_{AmR} = \frac{[A_m R]}{C_A^*} \quad [24]$$

$$x = \frac{x}{(D_A \tau)^{1/2}} \quad [25]$$

$$K = \frac{k_f C_A^*}{k_b}, \quad \beta = k_f C_A^* + k_b, \quad \gamma = \frac{\beta \Gamma m}{1 + K} \quad [26]$$

$$q = \frac{D_0}{D_A}, \quad r = \frac{D_R}{D_A}, \quad s = \frac{D_{A_m R}}{D_A}, \quad u = \frac{D_B}{D_A} \quad [27]$$

Equation [10] becomes:

$$\frac{C_A^*}{r} \frac{\partial C_A}{\partial t} = \frac{D_A C_A^*}{D_A r} \frac{\partial^2 C_A}{\partial x^2} - mk_f (C_A^b)^{m+1} C_A^m C_R + mk_b C_A^* C_{A_m R} \quad [28]$$

$$\frac{\partial C_A}{\partial t} = \frac{\partial^2 C_A}{\partial x^2} - mk_f r (C_A^*)^m C_A^m C_R + mk_b r C_{A_m R} \quad [29]$$

$$= \frac{\partial^2 C_A}{\partial x^2} - \gamma [K (C_A^*)^{m-1} C_A^m C_R + C_{A_m R}] \quad [30]$$

Similarly,

$$\frac{\partial C_0}{\partial t} = q \frac{\partial^2 C_0}{\partial x^2} \quad [31]$$

$$\frac{\partial C_R}{\partial t} = r \frac{\partial^2 C_R}{\partial x^2} - \gamma [K (C_A^*)^{m-1} C_A^m C_R + C_{A_m R}] \quad [32]$$

$$\frac{\partial D_{A_m R}}{\partial t} = s \frac{\partial^2 C_{A_m R}}{\partial x^2} + \gamma [K (C_A^*)^{m-1} C_A^m C_R + C_{A_m R}] \quad [33]$$

The new initial and boundary conditions become

Initial ($t = 0$)
 All x : $C_A = 1$, $C_0 = \frac{C_0^*}{C_A^*}$, $C_R = C_{A_m R} = 0$ [34]

Boundary:

$$t > 0, \quad x = 0: \quad C_A^s = C_B^s \exp [n_1 F(E - E_1^0)/RT] = \delta_1 \quad [35]$$

$$C_0^\sigma = C_R^\sigma \exp[n_2 F(E-E_2^0)/RT] = \delta_2 \quad [36]$$

$$\left(\frac{\partial C_A}{\partial X}\right)_{X=0} = \psi_A = -u \left(\frac{\partial C_B}{\partial X}\right)_{X=0} \quad [37]$$

$$q \left(\frac{\partial C_0}{\partial X}\right)_{X=0} = \psi_0 = -r \left(\frac{\partial C_R}{\partial X}\right)_{X=0} \quad [38]$$

$$t > 0, X \rightarrow \infty : \text{idem [34]} \quad [39]$$

The total electron flux, in dimensionless units, follows from [19]:

$$\psi = \psi_A + \psi_0 = i \left(\frac{r}{D_A}\right)^{1/2} (FAC_A^*)^{-1} \quad [40]$$

The dimensionless Cottrell fluxes for the two electron transfer processes are given by (see [21] and [22])

$$\psi_A \text{ (Cottrell)} = [(1 + u^{-1/2} \delta_1)(\pi t)^{1/2}]^{-1} \quad [41]$$

$$\psi_0 \text{ (Cottrell)} = [(1 + (q/r)^{1/2} \delta_2)(\pi t)^{1/2}]^{-1} \quad [42]$$

for any potential pulse magnitude. When the processes [7] and [8] are diffusion limited, [41] and [42] reduce to

$$\psi_A \text{ (Cottrell, D.L.)} = C_A^* \left(\frac{D_A}{\pi t}\right)^{1/2} \quad [43]$$

$$\psi_0 \text{ (Cottrell, D.L.)} = \alpha C_A^* \left(\frac{qD_A}{\pi t}\right)^{1/2} \quad [44]$$

so that the Cottrell currents are

$$i_A = F A C_A^* \left(\frac{D_A}{\pi t} \right)^{1/2} \quad [45]$$

$$i_0 = F A \alpha C_A^* \left(\frac{q D_A}{\pi t} \right)^{1/2} \quad [46]$$

Equations [30] - [33], taking the conditions [34] - [39] into account were solved by finite difference and orthogonal collocation techniques to provide the concentration profiles necessary to deduce the current response [40].

A value of m in equation [9] may be determined analytically when (a) both electron transfers are diffusion limited (high values of $-E$) and (b) k_f is very large. The boundary conditions then stipulate that C_A^σ and $C_0^\sigma = 0$. Two limiting cases will then exist that describe the total electron flux ψ_e to the electrode.

$$\langle 1 \rangle \text{ Assume } m\psi_0 > \psi_A \quad [47]$$

If $k \rightarrow \infty$ then C_A will be depressed to zero concentration wherever $mC_R > C_A$. Thus the value of

$$\left(\frac{\partial C_A}{\partial X} \right)_X = 0 \quad [48]$$

must be zero, since C_A^σ is also at zero (Figure 1). Hence A will not contribute to the electron flux ψ_e , and

$$\psi_e = \psi_0 \quad [49]$$

or

$$i = FA\psi_0 = FA\alpha C_A^* \left(\frac{q D_A}{\pi \Gamma} \right)^{1/2} \quad [50]$$

<2> Assume $m\psi_0 < \psi_A$

If $k \rightarrow \infty$, (Figure 2) the flux of A is reduced by m times the flux of O,
and

$$\psi_e = \psi_0 + (\psi_A - \psi_0) = \psi_A \quad [52]$$

or

$$i = FA\psi_A = FAC_A^* \left(\frac{D_A}{\pi \Gamma} \right)^{1/2} \quad [53]$$

If the electron fluxes given by [49] and [52] are normalized to ψ_0 , we
have

$$<1> \text{ For } m\psi_0 > \psi_A, \quad \frac{\psi_e}{\psi_0} = \frac{\psi_0}{\psi_0} = 1 \quad [54]$$

$$<2> \text{ For } \psi_A > \psi_0, \quad \frac{\psi_e}{\psi_0} = \frac{\psi_A}{\psi_0} = \frac{1}{\alpha q^{1/2}} = \frac{C_A^* D_A^{1/2}}{C_0^* D_0^{1/2}} \quad [55]$$

It will be of interest later to consider cases where the number of
electrons transferred to the O species is greater than 1, i.e.

$$n_2 > 1 \quad [56]$$

Therefore, proceeding as above, the general case for

$$A + e^- \rightleftharpoons B \quad [57]$$

$$O \rightleftharpoons n_2 e^- \rightleftharpoons R \quad [58]$$

$$mA + R \rightleftharpoons A_m R \quad [59]$$

leads to

$$\langle 1 \rangle \quad \frac{\psi_e}{\psi_0} = n_2 \text{ for } m\psi_0 > \psi_A \quad [60]$$

and

$$\langle 2 \rangle \quad \frac{\psi_e}{\psi_0} = \frac{n_2 \psi_0 + (\psi_A - m\psi_0)}{\psi_0} = \frac{(n_2 - m) \psi_0 + \psi_A}{\psi_0} \quad [61]$$

$$= (n_2 - m) + \frac{1}{\alpha q^{1/2}} = (n_2 - m) + \frac{C_A^* D_A^{1/2}}{C_0^* D_0^{1/2}} \quad [62]$$

$$\text{for } \psi_A > m\psi_0 \quad [63]$$

Hence a plot of the normalized current $\frac{\psi_e}{\psi_0}$ vs. $\frac{1}{\alpha q^{1/2}}$ has the form shown in Figure 3. The point of intersection of the two linear portions will be when

$$m\psi_0 = \psi_A \quad [64]$$

At that point

$$m = \frac{\psi_A}{\psi_0} = \frac{1}{\alpha q^{1/2}} = \frac{C_A^* D_A^{1/2}}{C_0^* D_0^{1/2}} \quad [65]$$

The y intercept for the extrapolated $\frac{\psi_e}{\psi_0}$ line for case <2> will be at

$$\frac{\psi_e}{\psi_0} = (m - n_2) \quad [66]$$

It should be pointed out that there are other general shapes for the plot in Figure 3, depending on the values of n_2 and m . The rules for the analysis treatment are still the same.

SIMULATION

(A) FIRST ORDER KINETICS in C_A and C_R (i) $E_2^\circ > E_1^\circ$

From equation [26], we have the relation between the real rate constants, equilibrium constant, dimensionless parameters, and pulse length:

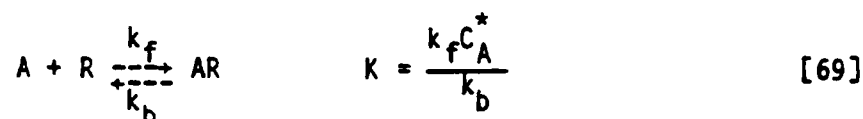
$$k_f = \frac{\gamma K}{C_A^b \Gamma m}; \quad \gamma = \frac{C_A^b \Gamma m k_f}{K} \quad [67]$$

$$k_b = \frac{\gamma}{\Gamma m}; \quad \gamma = \Gamma m k_b \quad [68]$$

The results presented in this section will be for a measurement made at 10% of the total chronoamperometric pulse time. Figure 4 shows the simulated normal pulse voltammograms for a fixed concentration of species A as a function of the O concentration. In this case $\gamma = K = 0$, so that ψ_A and ψ_0 are given by the Cottrell relations [41] and [42]. The

diffusion currents represent simple uncoupled charge transfers. The concentration increments of the O species are equal at $0.20 C_A^b$ units, and range (bottom to top) from 0.0 to $4.0 C_A^b$ units. We assume $D_A = D_O$ for simplicity.

Figure 5 represents the same system now perturbed by the kinetic reaction



The reaction [69] is first order in each reactant A and R. In the Figure, $\gamma = 4.0$ and $K = 1.0$. It is seen that at all concentrations $C_O^* > 1.0 C_A^*$, the incremental change in the flux at high negative potentials is precisely the same as in Figure 4. The absolute value of the total flux is decreased by an amount equal to ψ_A . At all concentrations $C_O^* < 1.0 C_A^*$, it is seen that the incremental changes in total flux at high negative potentials have been reduced to very small levels, but are still equal. The absolute values of the fluxes lie between $\psi_e = \psi_A + 0.2 \psi_A$ and $\psi_e = \psi_A$. In addition, peaks and dips have appeared in the voltammetry in the region of the second wave and plateau. The height and depths of these features, as well as the potentials of the critical points are functions of γ , K and the concentration ratio.

As the values of γ and K are increased, it is found that the peaks and dips level out, and the fluxes for the $C_O^* < 1.0 C_A^*$ decrease to a limiting value of $\psi_e = \psi_A$, as is called for by equation [52]. For $C_O^* > 1.0 C_A^*$, it is found that $\psi_e = \psi_O$ as is called for by equation [49]. It is pointed out here that for $C_O^* > 1.0 C_A^*$, the results for the limiting ψ_e at high negative potentials are the same for all values of $\gamma \gtrsim 2.0$ and $K \gtrsim 1.0$.

It is apparent from equations [49] and [52], for the first order case (each reactant), that the lowest observed diffusion current will never be less

than that corresponding to ψ_A (Cottrell).

$$(ii). E_2^* = E_1^*$$

The results here are virtually the same as for the previous case, except that there is only one voltammetric wave (Figure 6). The absolute value for the electron flux ψ_e for large values of γ and K are again given by [49] and [52].

$$(iii). E_2^* < E_1^*$$

In this case (Figure 7), O is reduced before A. Therefore, it is the products of the first electron transfer that are involved in the kinetic reaction instead of the reactant. The diffusion controlled portion of the first voltammetric wave is always only determined by the flux of O to the surface and will therefore now be subject to depression by the kinetic reaction. The height of the second electron transfer wave will be strictly determined by the homogeneous kinetics, and again is given quantitatively by [49] and [52] for polarograms for this case. The half wave potentials are shifted by amounts governed by the ratios of the surface concentrations of each redox pair, just as they are in the other cases.

(B). Multi-Order Kinetics in A and R

The same general conclusions can be made for this case as were made for (A) i, ii, and iii above. For high values of γ and K , the diffusion limited current at high negative potentials is governed by the relations

$$\psi_e = n_2\psi_0 \text{ for } m\psi_0 > \psi_A \quad [70]$$

and

$$\psi_e = (n_2 - m) \psi_0 + \psi_A \quad \text{for } \psi_A > m\psi_0 \quad [71]$$

(see [60] and [61]).

An important feature here is, that when $\psi_A > m\psi_0$, and $m > n_2$, it is possible (cf $m = 3$, $n_2 = 1$, $\psi_A = 0.31$, $\psi_0 = 0.1$) for the net current flux ψ_e to be less than ψ_A . Hence plateaus at levels less than that of ψ_A are observed (Figure 8).

Results for the reaction



with $C_A^b = C_O^b$ as a function of C_A^b is shown in the Figure to demonstrate the diversity in possible voltammetric shapes for the same system. The kinetic parameters here are $\gamma = 4.0$, $K = 1.0$ and $E_1^\circ < E_2^\circ$. At high concentrations, two maxima and a minimum are produced before diffusion limiting flux is attained. At lower concentrations, one maximum is seen, and at even lower concentrations, there are no inflections. An example of this type of behavior is presented in part II of this series (3).

ACKNOWLEDGEMENTS

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FIGURE LEGENDS

Figure 1. Typical concentration profiles for the case $m\psi_0 > \psi_A$, $k = \infty$

Figure 2. Typical concentration profiles for the case $m\psi_0 < \psi_A$, $k = \infty$

Figure 3. Plots of the normalized current function $\frac{\gamma}{\psi} e$ vs. the normalized bulk concentration - diffusion coefficient ratio $(\alpha^2 q)^{-1/2}$ for: (A) $m\psi_0 > \psi_A$; and (B) $m\psi_0 < \psi_A$.

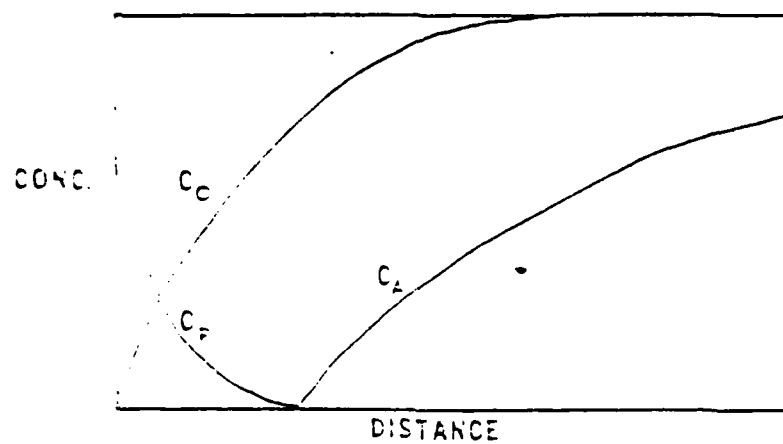
Figure 4. Simulated normal pulse voltammograms for two electroactive species A (first wave) and O (second wave) with no kinetic complications. Bottom voltammogram $C_0 = 0.0$. In each successive voltammogram, the concentration of O is incremented by $0.2 C_A$ units. The top curve corresponds to $C_0 = 4.0 C_A$. The diffusion coefficients are assumed equal.

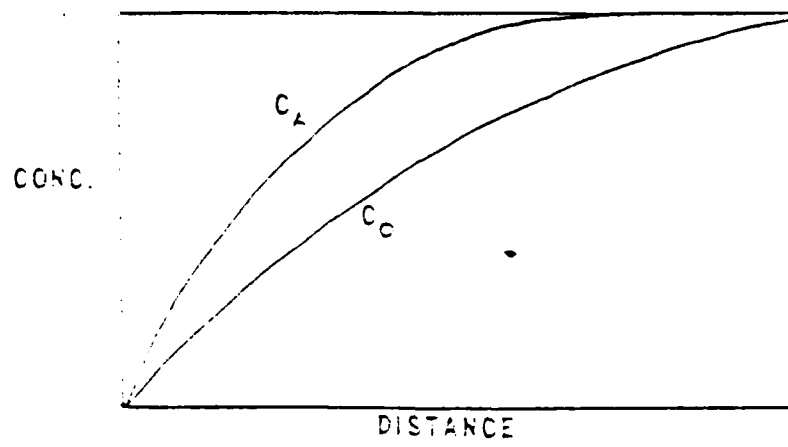
Figure 5. As Figure 4 with $\gamma = 4.0$ and $K = 1.0$.

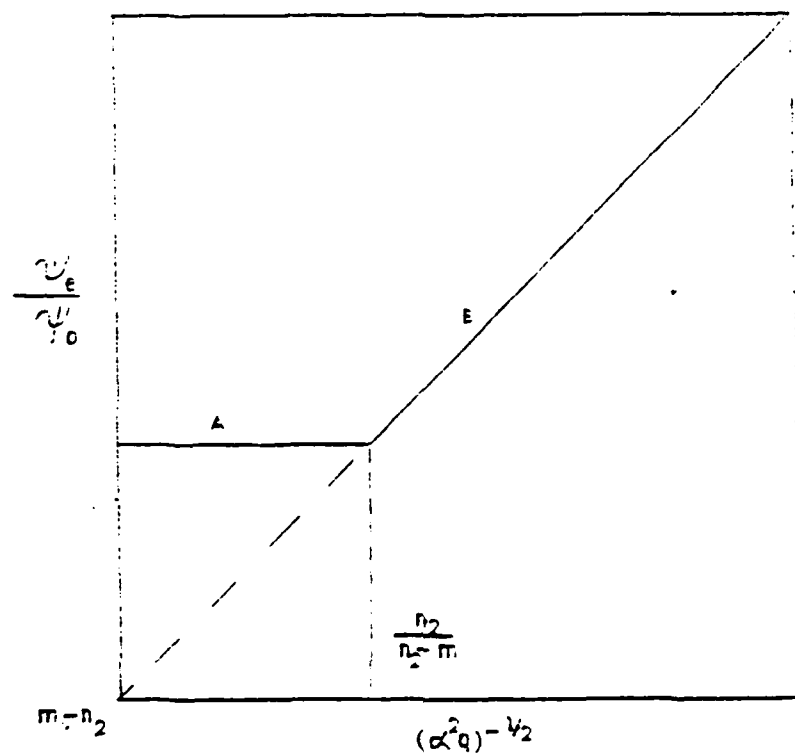
Figure 6. Simulated normal pulse voltammograms for the case $E_1^\circ = E_2^\circ$. The concentration of C_A is held fixed and the concentration of C_0 is varied (bottom to top) from 1.0 to $3.8 C_A$ in increments of $0.4 C_A$. The superimposed curve (for clarity) is for no kinetic reaction in a mixture of A ($C_A = 1.0$) and O ($C_0 = 4.0 C_A$).

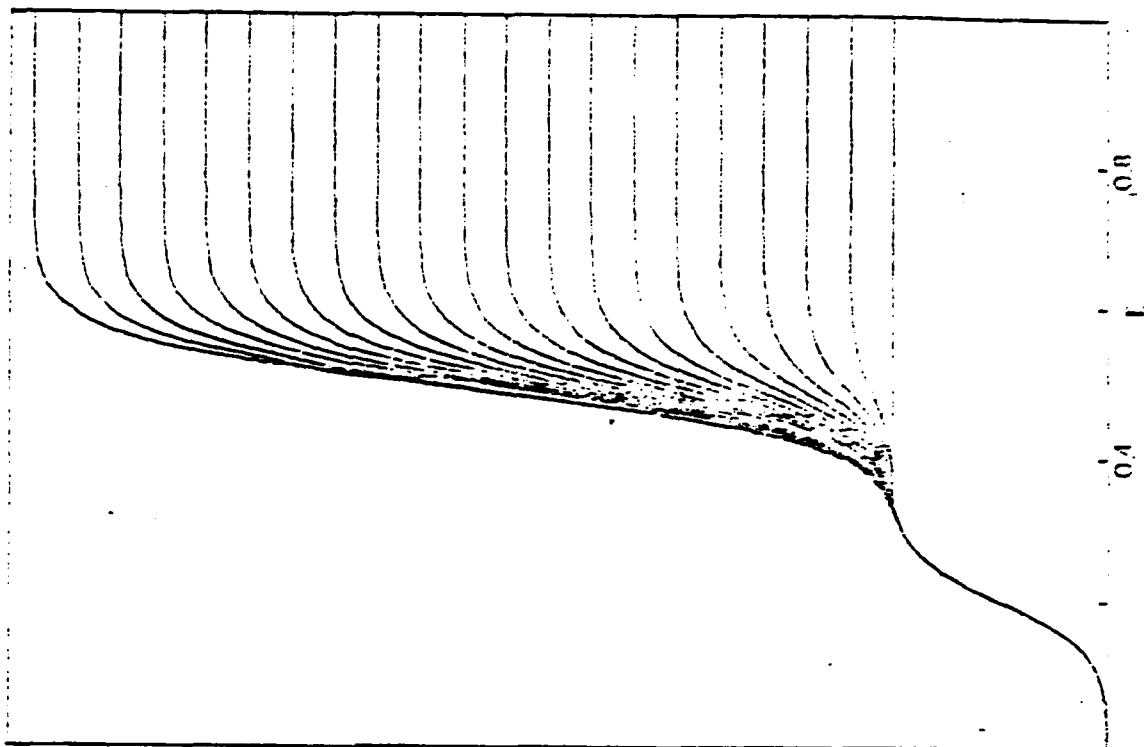
Figure 7. Simulated normal pulse voltammograms for the case $E_2^\circ < E_1^\circ$. The concentration of C_A is held fixed and the concentration of C_0 is varied (bottom to top) from 1.0 to $3.8 C_A$ in increments of $0.4 C_A$. The superimposed curve for clarity, is for no kinetic reaction in a mixture of A ($C_A = 1.0$) and O ($C_0 = 4.0 C_A$).

Figure 8. Simulated normal pulse voltammograms for the case of multi-ordered kinetics; $3A + R \rightleftharpoons A_3R$, $C_A = C_0$, $\gamma = 4.0$, $K = 1.0$, $E_1^\circ < E_2^\circ$. From bottom to top: concentrations = 0.25 , 0.50 , 0.75 , 1.0 , 1.5 , 2.0 , 2.25 , and 2.5 .

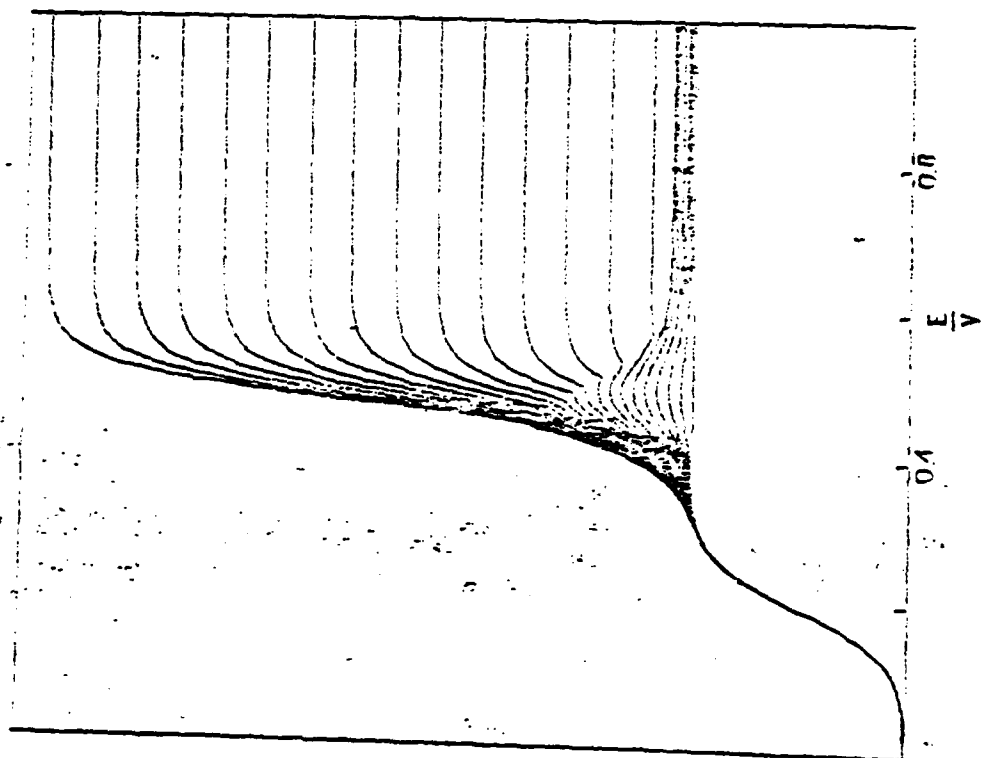








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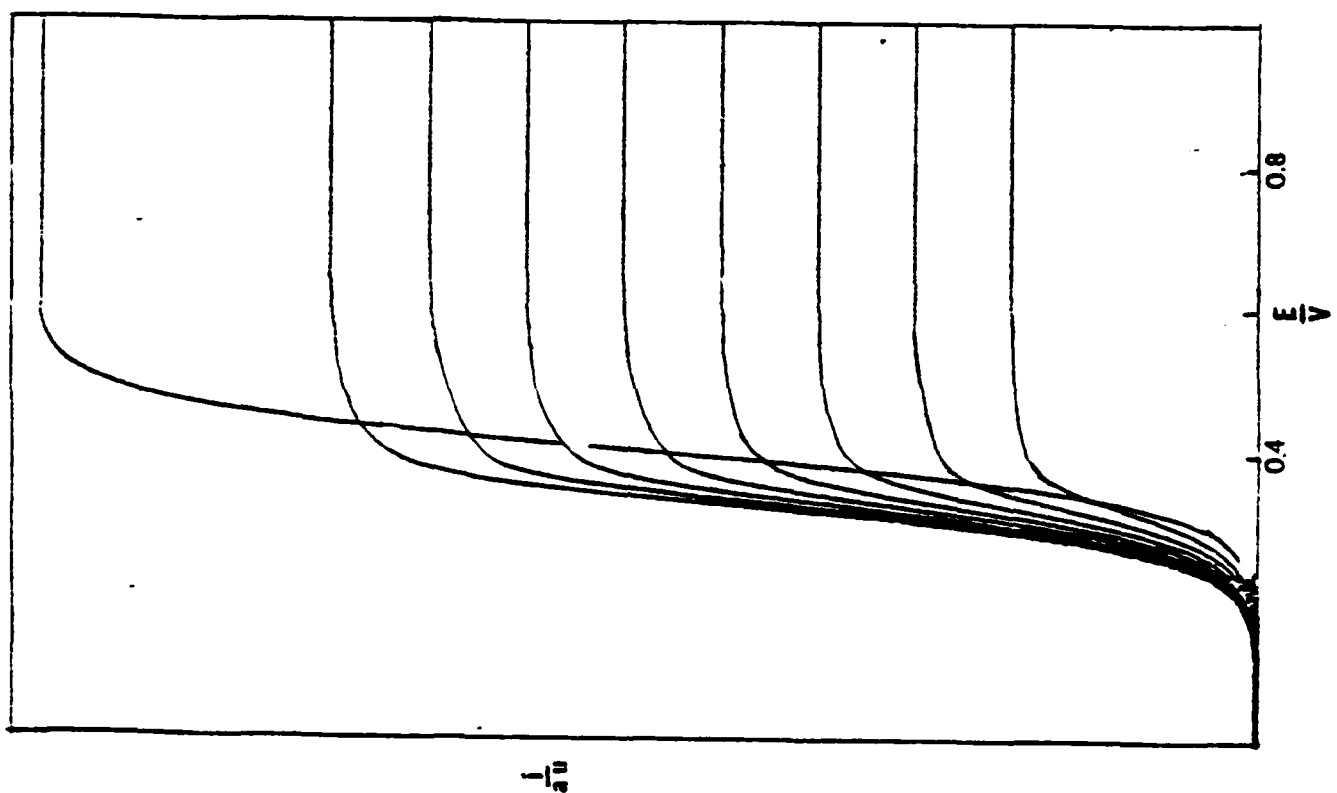


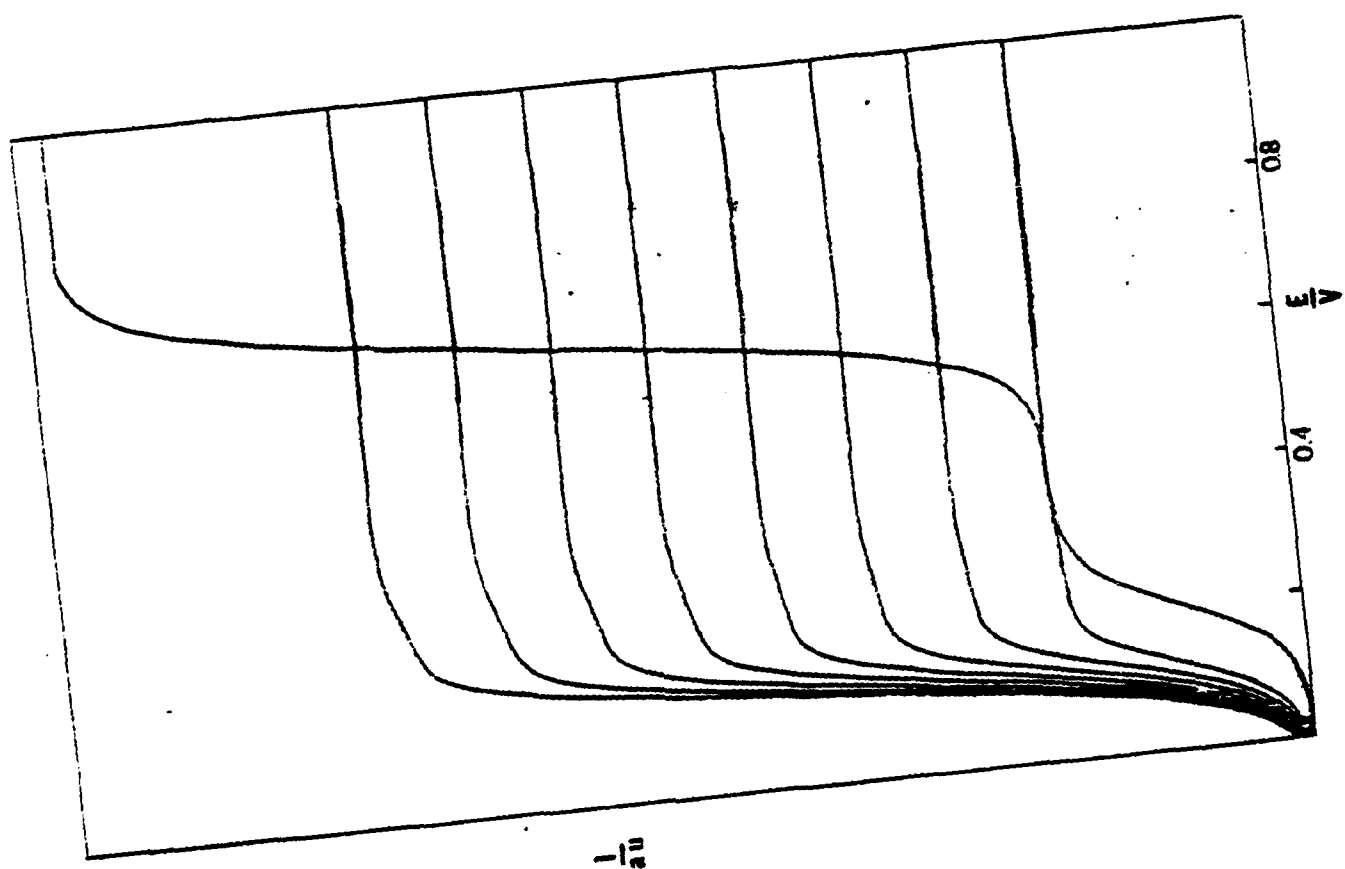
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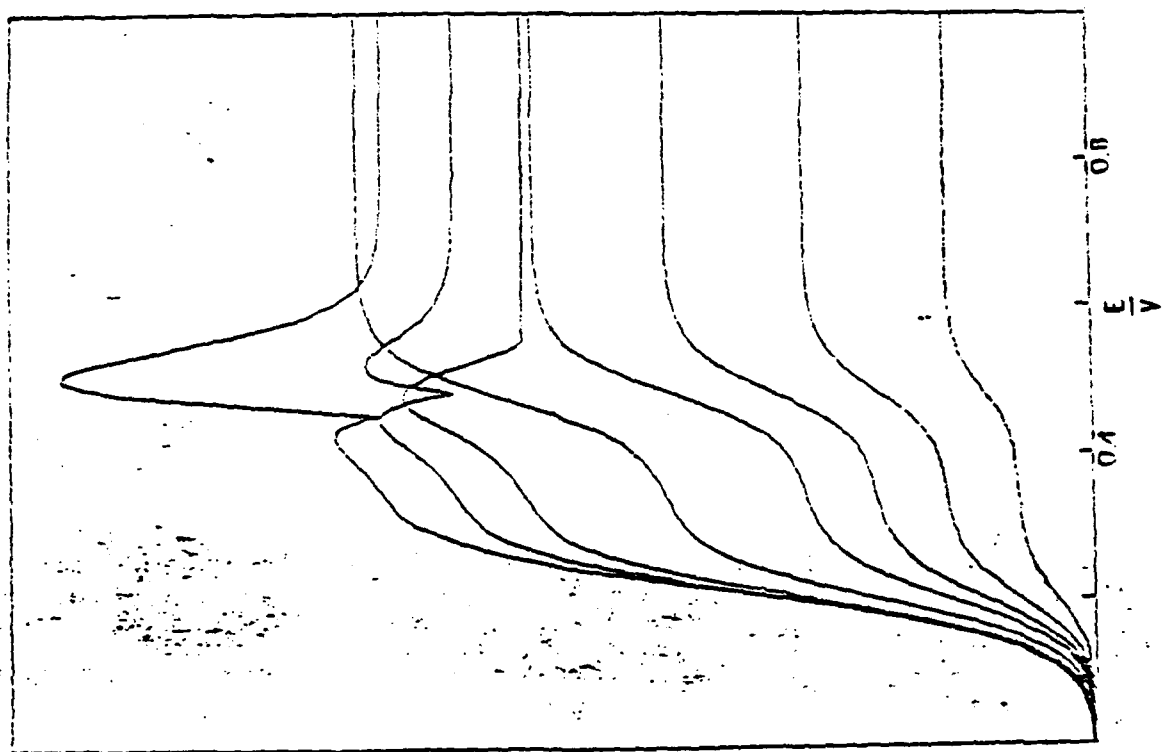
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